Ion Association Near Critical Points of Ionic Fluids

V.C. Weiss and W. Schröer
Institut für Anorganische und Physikalische Chemie
Universität Bremen
D-28334 Bremen, Germany

H. Weingärtner
Physikalische Chemie II
Ruhr-Universität Bochum
D-44780 Bochum, Germany

We use several Debye-Hückel-based theories in order to investigate ion association near the critical point of the hard sphere ionic fluid. We examine the degree of dissociation and its consequences for thermodynamic properties and the coexistence curve. In detail, we consider a pairing theory based on Ebeling's definition of the association constant for ion pairing, and its extensions for ion pair - free ion interactions by Fisher and Levin and for ion pair - ion pair interactions by Weiss and Schröer. The effect of ion pairing on the dielectric constant is also discussed. Results are compared with experimental data for coexistence curves, electrical conductances, and dielectric constant behavior of real ionic fluids showing liquid-liquid phase separation. The results indicate the importance of pair formation at low ion densities and give evidence for a redissociation of ion pairs at higher ion densities. This transition is reflected by a comparatively sharp increase of the electrical conductance from almost non-conducting to highly conducting states. The gross features of this transition aredescribed. Specifically, it is shown that there is a peak in the temperature dependence of the isobaric (and isochoric) heat capacity. The significance of this transition in relation to the criticality of ionic fluids is discussed.